The Ionization of Phosphonium Iodide

by

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A.B. University of Kansas, Fall, 1924

Submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Master of Arts.

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May 29, 1926

The Chemistry Building

To H. P. Cady, Ph. D.
Whose Inspiration and Excellence as an Instructor
Caused Me to Change my Career
from
Medicine to Chemistry
and
Under whose Untiring Guidance
My Investigation was Completed
This Work is Affectionately Dedicated

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The Office

The Ionization of Phosphonium Iodide

Phosphonium Iodide is a white, sal-ammoniac-like, crystalline substance at ordinary temperatures. It is very deliquescent and since it decomposes into phosphine and hydrogen iodide upon the addition of water, according to the equation

$$(PH_4I + H_2O = PH_3 + HI + H_2O)$$

it is impossible to use water as a solvent to test its ionization. McIntosh and Steele[°] made tests upon the liquified hydrogen compounds of phosphorous, sulphur, and the halogens as conducting solvents, but in no accounts of their experiments was I able to find indication that they had used phosphonium iodide as a salt dissolved in any of these solvents. So it is my purpose to try to dissolve phosphonium iodide in pure liquid ammonia, liquid phosphine, liquid hydrogen iodide, and possibly in liquid hydrogen fluoride if I can procure the necessary platinum apparatus to prepare the hydrogen fluoride.

Phosphohiumjodid, PH_4J.[1]
Jodphosphonium

Preparation according to Baeyer

In a medium-sized tubulated retort, place dry carbon disulfide; dissolve in it 100 grams phosphorus (yellow) and cool while dropping in 175 grams of iodine. Then distill off the CS_2 and remove the last remnant of the same by means of a dry current of CO_2 while gently warming the retort. After cooling, a long, wide, thin-walled glass tube is arranged in place of the condenser and the end of the tube is connected with a gas pipe which dips into a flask partly filled with some water, but does not touch the surface of the water. Then drop 50 grams of water into the phosphorus tri-iodide (a small portion at a time) through a funnel drawn out at the end. With every addition of the water there is a lively reaction. Phosphonium iodide condenses on the inside of the retort and in the wide glass tube, and a small quantity of hydrogen iodide also escapes which is absorbed by the water mentioned above. After the entire quantity of water has been added the retort is warmed,

°McIntosh and Steele, Proceedings of the Royal Society of London, London, 1904, Vol. 73, p. 450; Chemisches Central - Blatt. 1904, II, p.398

[1]Dr. Ludwig Vanino, Handbuch der Präparativen Chemie, 1913 I, pp. 203, 204

The Preparation of Phosphonium Iodide.
Fig. 1.
Drawing from Vanino

C = CO_2 container
R = PH_4I generator
A = Air condenser on which PH_4I sublimed
F_1 = Receiving flask
F_2 = Water container for absorption of HI

Handbuch: Vanino I, p. 203

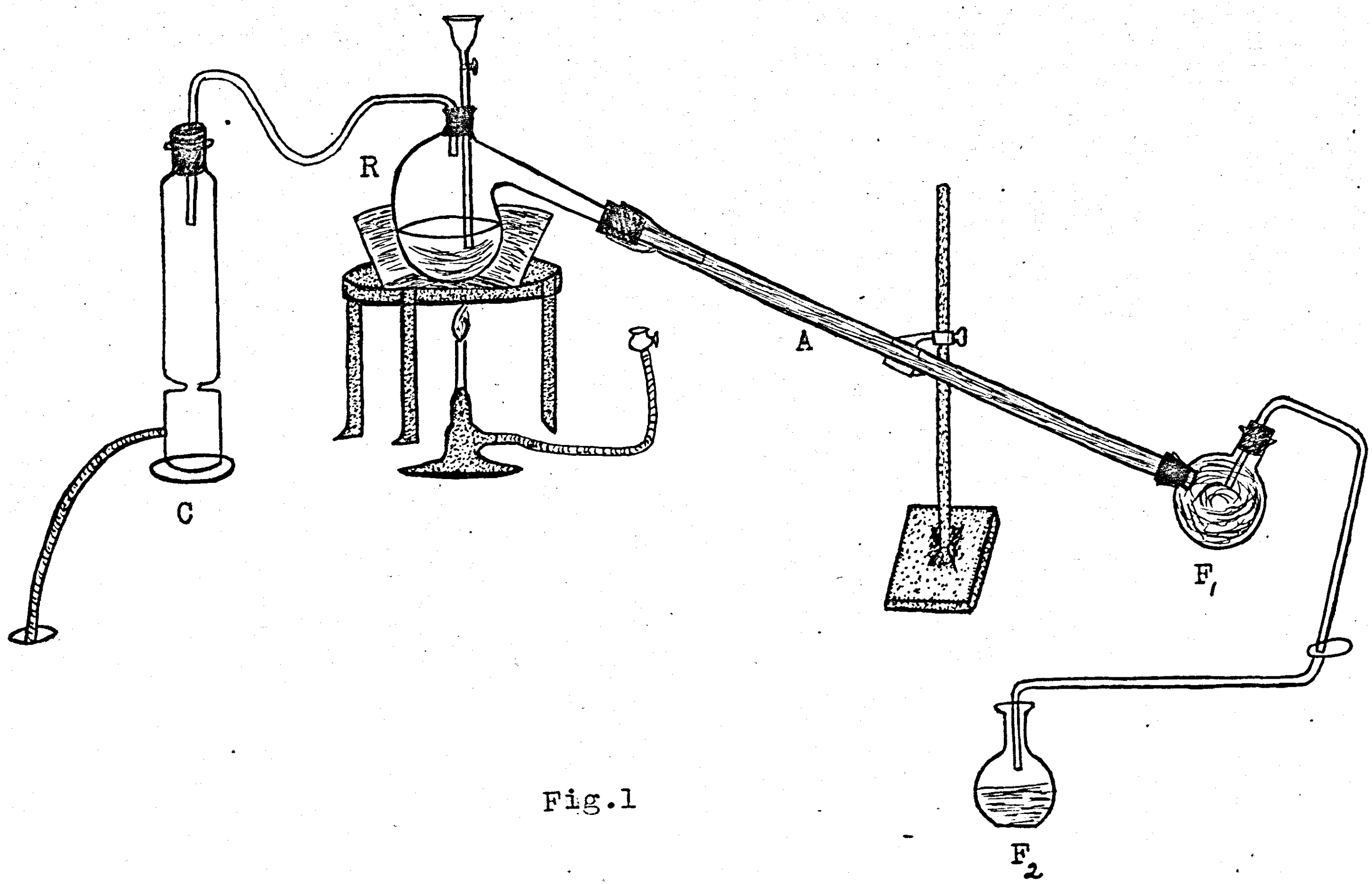


Fig.1

gently at first, then to dull redness and the phosphonium iodide is driven completely into the glass tube. After cooling, break the tube and remove the thick crust of phosphonium iodide which resembles sal-ammoniac; the quantity should be about 120 grams according to calculations.

"Properties: Large, clear adamantine-lustered crystals which sublime at ordinary tempeeratures. B.P. 80°C. By gentle warming the crystals sublime here and there in a closed receptacle without melting."[2]

Phosphonium iodide was discovered by Labillardiere and Gay Lussac and more fully examined by Serullas and H. Rose.[3] It may be formed (1) by bringing together PH_3 and HI as gases, or in concentrated aqueous solutions, (2) by the action of gaseous PH_3 on I_2, (3) by the action of red P on concentrated HIAq. at 160°C., (4) along with P_2I_4 by the action of HI gas on P at ordinary temperature, (5) by the action of a little H_2O on PI_3 as was done in this experiment, (6) by the reaction of HI on H_3PO_2 and then warming the product in CO_2. Hofmann[4] expressed the reaction for its preparation used above thus:

$$13P + 9I + 21H_2O = 7PH_4I + 3H_4P_2O_7 + 2HI$$

Roscoe and Schorlemmer expressed the reaction as:

$$5I + 9P + 16H_2O = 5PH_4I + 4H_3PO_4$$ [5]

They state that an excess of phosphorus is in practice employed because a part of this substance is converted during the reaction into the red modification. The formation of the hydriodic acid which escapes is due to the decomposition of the phosphonium iodide in the presence of warm water. Although phosphonium iodide boils at about 80°C., it easily vaporizes at a lower temperature. It is used in the laboratory as a powerful reducing agent as well as for the preparation of many organic phosphorus compounds. According to Watt the molecular weight of this compound has not been determined, but it is believed to be similar to NH_4I and is given the formula PH_4I.

It reacts in the following manner:

1. With C compounds it acts as a very energetic reducing agent and is much used in preparing phosphines.
2. Decomposes rapidly with H_2O or alkali solution, evolving non-inflammable PH_3.

[2] Handbuch; Vanino I, p.204
[3] Pattison Muir, Watts' Dictionary of Chemistry, 1914, IV, p. 123
[4] Ibid., p.124
[5] Roscoe and Schorlemmer, A Treatise of Chemistry, 1905, I, p. 624

3. With ethyl-alcohol it forms Et.I and PH_3 and if reaction takes place in a sealed tube PEt_3 and PEt_4I are produced.
4. With phosphorus trichloride it forms P_2I_4, HCl, PH_3, and solid P_2H.
5. PH_4I is inflamed by contact with many concentrated acids, e.g. HNO_3, HCl, HBr, HI.

6. $PH_4I + \begin{cases} ClO_3 \\ BrO_3 \\ IO_3 \end{cases} \rightarrow$ inflammable at ordinary T.

7. $PH_4I + AgNO_3 \rightarrow AgI + Ag_3PO_4$

8. $PH_4I + Ag_2O \rightarrow AgI + P_2H_4 + PH_3$

9. $PH_4I + HgCl \rightarrow HgI_2 + HCl + PH_3$

10. $PH_4I + HgBr_2 \rightarrow HgI_2 + PH_4Br$

11. $PH_4I + \begin{cases} Hg(CN)_2 \\ KCN \end{cases} \rightarrow \begin{cases} HgI_2 \\ KI \end{cases} + HCN + PH_3$

12. $3PH_4I + 3SbCl_5 \rightarrow SbI_3 + 2SbCl_3 + 9HCl + PH_3 + P_2$

13. $4SnCl_4 + 4PH_4I = SnI_4 + 3SnCl_2 + 10HCl + 2PH_3 + P_2$

14. $6SnCl_4 + 6PH_4I = 3SnI_2 + 3SnCl_2 + 18HCl + 2PH_3 + 4P$

15. $4PH_4I + 8COCl_2 = 16HCl + 8CO + P_2I_4 + 2P$

16. $4PH_4I + 3CS_2 = P(CH_3)_3HI + 3H_2S + 3PSI$

17. Does not react below 140° with CS_2, but at higher temperatures, 140° and above, it reacts in the following manner:

$$3CS_2 + 4PH_4I = P(CH_3)_3HI + 3H_2S + 3PSI$$

18. HgCl yields HgI_2, HCl and PH_3 with PH_4I.

19. HgBr decomposes with PH_4I into HgI_2 and PH_4Br which has however still PH_4I mixed with it.

20. $3SbCl_5 + 3PH_4I = SbI_3 + 2SbCl_3 + 9HCl + PH_3 + P_2$ [6]

[6] C. Friedheim, Gmelin-Kraut's Handbuch der anorganischen Chemie, 1907, *I-3*, p. 381

In my preparation of phosphonium iodide Vanino's method[7] was modified somewhat. Natural gas from the gas mains was used instead of CO_2. The whole system was kept in an atmosphere of natural gas as soon as all the iodine had been added. PH_4I was prepared three different times. After the beautiful white crystals had sublimed on the air condenser it was thought probable that from heating the air condenser the PH_4I could all be driven into the receiver R, but although the cork connections seemed very tight the blaze attacked the PH_4I, which decomposed with a loud report and the flame seemed to rush the entire length of the dondenser. The PH_4I which did remain turned brown, due to coloration by free iodine.

Liquid ammonia was prepared from the commercial liquid ammonia by using a liquid air condenser apparatus which permitted the liquid ammonia to distill and leave the water behind as ice when the temperature was raised to the boiling point of ammonia. Then, since sodium turns anhydrous ammonia a deep blue, the ammonia was tested in this way and found to be pure. A small portion of phosphonium iodide was placed in a pyrex test-tube and the test-tube was inserted in liquid air. The phosphonium iodide was cooled in this manner so that violent reaction would not be due to difference of temperature between solute and solvent. The PH_4I was then dropped into the liquid ammonia. Large bubbles of gas were evolved and the PH_4I disappeared from sight. The question was, "Were these bubbles phosphine, and if not, what were they?" The liquid ammonia was then evaporated until the residue did not smell of ammonia, and tests were made upon the residue. Ammonium iodide would dissolve readily in H_2O without evolution of ammonia. If water were added to phosphonium iodide it would give off gaseous PH_3 and HI. A small portion of the residue was tested with water. The solute dissolved with no evolution of gas. This solution was placed in a small beaker and a watch-glass containing a piece of moistened litmus was placed on the under side. The beaker was heated slightly, the litmus turned a deep blue, indicating the presence of NH_3.

[7] Handbuch: Vanino. I, p. 203-204

Another small portion of the residue was dissolved in chlorine water and a few drops of the resulting solution placed in starch solution. The starch turned a deep blue, indicating the presence of free iodine. It was therefore concluded that the residue was ammonium iodide and that the gas evolved when the phosphonium iodide was placed in the liquid ammonia must have been phosphine. It might be added that the ammonia container was carefully dried by means of ethyl-alcohol, ether, and by drawing dry air through it; and also that the ammonia was allowed to vaporize partially and fill the entire Dewar flask, and the tube containing the phosphonium iodide by placing a piece of loose cotton in the neck of the Dewar and allowing the water vapor, if there was any, to be completely replaced by ammonia vapor before the addition of the solute to the solvent, after the solute had been cooled in liquid air. So, likewise with ammonia as with water, it was found impossible to use liquid ammonia as a solvent to test the ionization of phosphonium iodide.

Ammonia, NH_3, is by far the most important of the compounds of nitrogen and hydrogen. It was first obtained in the gaseous state by Priestly, 1774.[8] The yearly production of NH_3 and its salts is equal to 260,000 tons of ammonia. It is present in very small quantities in the air and in all rain and river waters. It may be prepared directly from the elements when heated or by means of the electric spark. Water acts upon nitrides forming ammonia and the hydroxide of the metal. Animal refuse, including hair, feathers, hides, etc., when heated, give off some of the nitrogen in the form of ammonia. Decaying animals and vegetables give off ammonia. Liquid ammonia, a very common article of commerce, is compressed and shipped in strong iron cylinders.[9] This was the source of ammonia used in my experiment. It was dehydrated, as noted above, with metallic sodium.

Liquid ammonia boils at $-33.5^\circ C$. It is a colorless, very mobile liquid which freezes to a white crystalline solid at $-77^\circ C$. It has a density equal to .677 at its B. P. It is a very good solvent for many substances. When salts are dissolved in liquid ammonia some are dissociated similarly as in water. The ions travel faster in ammonia than in water.[10]

[8] Roscoe and Schor., I, p. 493
[9] Hamilton P. Cady; General Chemistry, 1916, p.195
[10] Roscoe and Schor., I, p.498; H. P. Cady, Inorganic Chemistry, 1912, p. 230

The Preparation of Phosphine
Fig. 2

A rough sketch of the apparatus used for the first preparation of hydrogen phosphide. Tube, T,^{1} was surrounded by a Dewar containing liquid ammonia. T^2 by one containing liquid air.

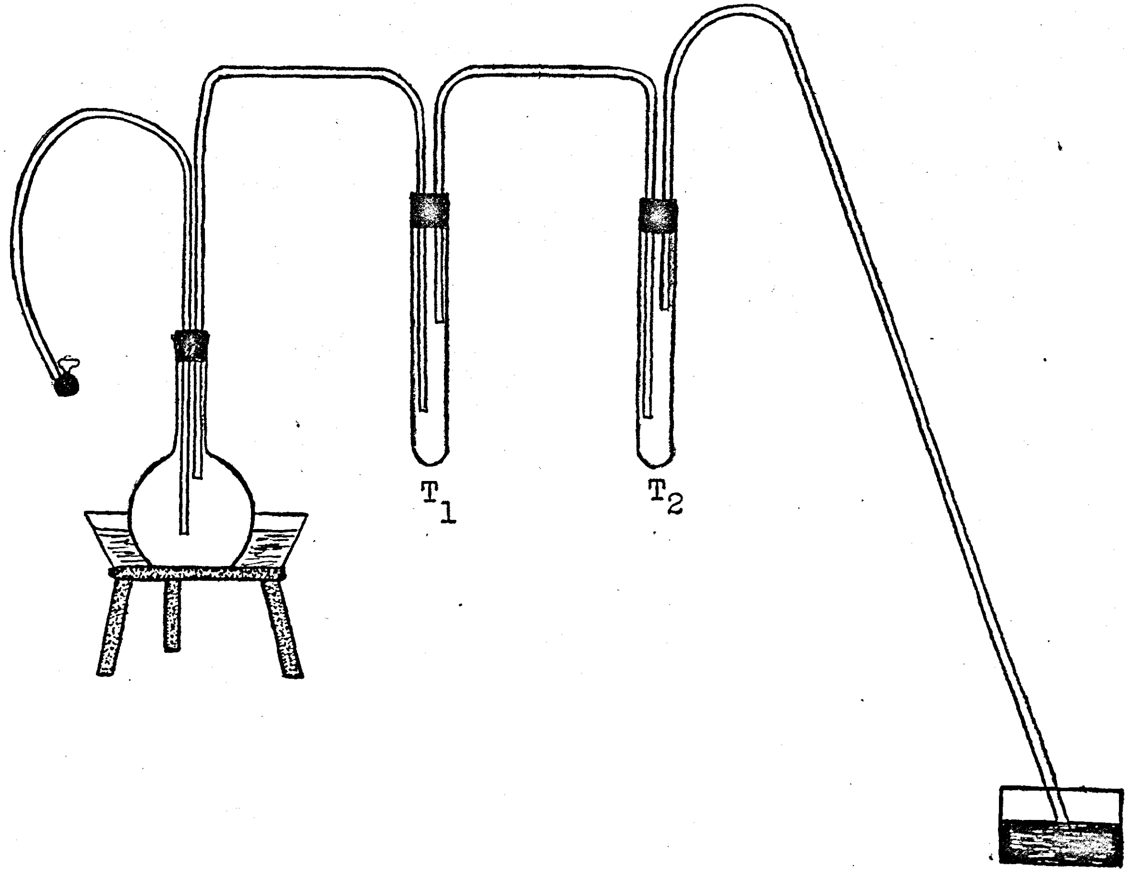


Fig. 2

So an electrolyte formed in this manner may be a better conductor of electricity than it would be using H_2O as a solvent.

The most important chemical property of ammonia is its ability to combine directly with acids to form salts,[11] This process is generally reversed if the salt so formed is heated to a sufficiently high temperature. When ammonia dissolves in water a part of it combined for the formation of ammonium hydroxide, according to the equation:

$$NH_3 + H_2O = NH_4OH$$

Ammonium salts, when dissolved in liquid ammonia, act in almost every way as acids do in water. Such solutions attack metals with the evolution of H_2 in the formation of a salt and metal.[12] It is probably due to the fact that ammonia resembles water very closely that the phosphonium iodide decomposed when brought in contact with the liquid ammonia.

Preparation of the Non-Spontaneously Combustible PH_3.[13]

1. One proceeds as in I and separates the spontaneously combustible part.

I. Preparation of a spontaneously combustible phosphorus-hydride mixture.

A spontaneously combustible mixture of phosphorus hydrides which owes its spontaneous combustibility to the presence of liquid hydrogen phosphide, is prepared by heating yellow phosphorus with aqueous alkali. One proceeds according to Arendt as follows:

Fill a tubulated retort half-full of dilute KOH, put a piece of yellow phosphorus the size of a pea through the tube, close it with a cork having an inlet tube, shove a pinch cock over the tube and join it to a hydrogen generator (take away the stop cock on application of a Kipp generator). The neck of the retort is closed with a bent outlet tube at least 5 mm. wide, which dips into a shallow pan of H_2O.

[11]General Chemistry, p. 197
[12]From notes taken from Dr. Franklin's lecture on liquid ammonia before the K. U. Chemistry Club.
[13]Handbuch: Vanino, I, p. 172

As soon as the air is driven out by the hydrogen, the cock of the Kipp apparatus is closed (or rather wait until the acid in the gas generator is exhausted, therefore do not use too much acid) and the retort is heated carefully.

When the liquid is warm and the phosphorus melts the generation of the gas begins and the bubbles ignite (as soon as the hydrogen is driven out) on contact with the air with a voluminous, very luminous flame from which a smoke ring rises becoming larger and larger in ascending.

The experiment is dangerous, even if the heating is carefully and quite prudently carried out; the bubbles should follow each other slowly, the generation of the gas dare not cease entirely, for if the H_2O from the trough backs up and the layer above the outlet tube is not deep enough, air rushes into the apparatus, which causes an explosion.

In order to end the experiment the hydrogen stream is started by pouring some acid into the gas generator, which drives the hydrogen phosphides from every part of the apparatus (air is permitted under no circumstances to get in). Only when the phosphorus is thoroughly hardened should the apparatus be taken apart. The phosphorus is washed after ending the experiment, since otherwise - especially in summer - it forms hydrogen phosphide.

In order to remove the gas from the spontaneously combustible P_2H_4 (liquid), join the neck of the retort with the inlet tube of a Woulff bottle (or wash bottle) half-filled with HCl whose outlet tube (rubber) is led into a pneumatic trough, in which, upon the bridge, stands a cylinder filled with H_2O. One, as before, drives out the air from the apparatus with H_2, warms the retort and leads the gas first into a vessel filled with H_2O whose contents correspond (about) to the free content of the fluid in retort and wash bottle; and then, after one assumes that the hydrogen is driven out, into the cylinder filled with H_2O. Also by washing with alcoholic KOH the spontaneously combustible P_2H_4 separates. From Dumas) it is concluded that 62.5 Vol. % H is generated from P and KOH; from von Hoffmann.

The Preparation of Phosphine
Fig. 3

A sketch of the apparatus used resulting in the successful preparation of phosphine.

F_1 - Phosphine generator
T_1 - T-tube dipping into Hg, serving as controlling valve
F_2 - Water condenser
T_2 - Water condenser and condenser of yellow solid
T^3 - Condenser of yellow solid also
T_4 - Condenser of solid phosphine
T_5 - Condenser of liquid phosphine
C - Crystallizing dish containing Hg covered with H_2O
D_1 - Dewar containing liquid NH_3
D_2 - Dewar containing liquid NH_3
D_3 - Dewar containing liquid air
D_4 - Dewar containing liquid NH_3
I - Inlet tube for CH_4

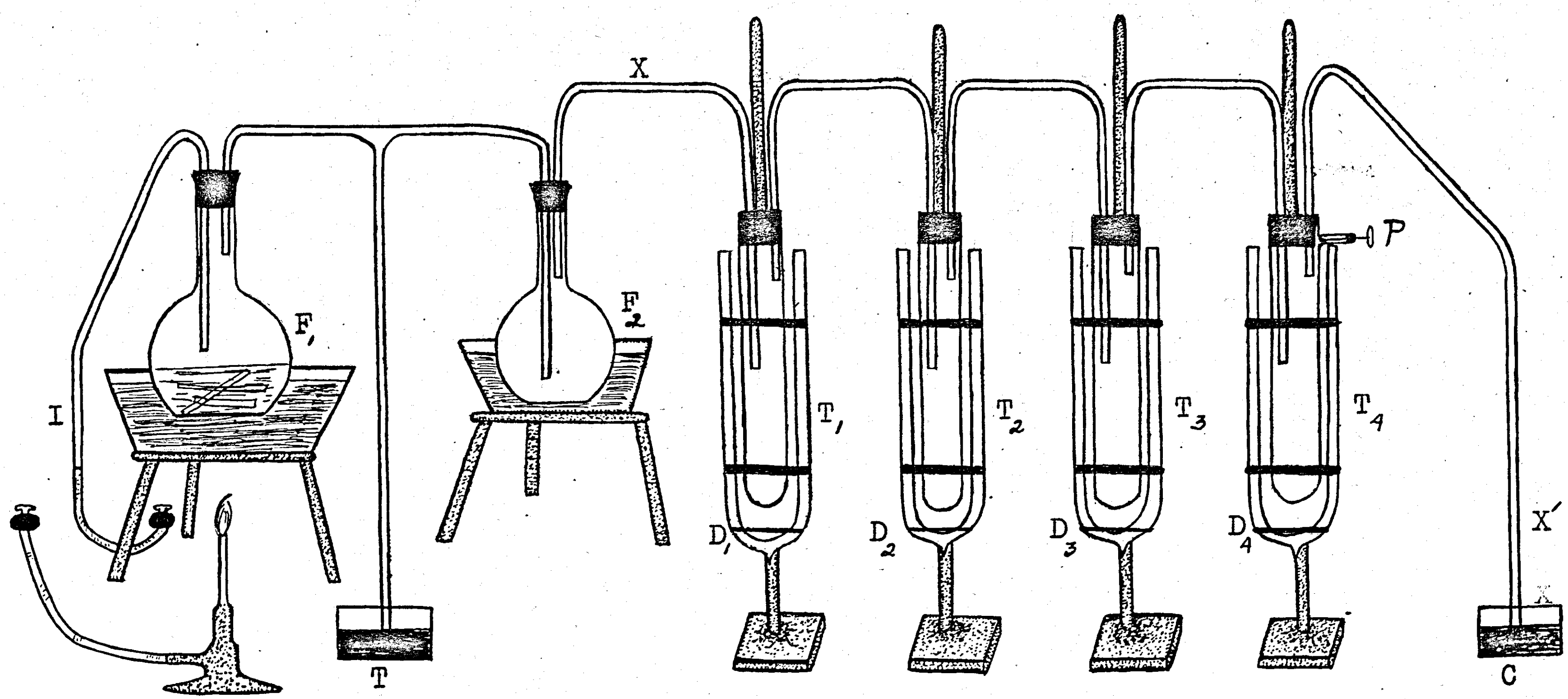


Fig. 3

Since most of the PH_4I was decomposed by the explosion mentioned previously;it was made a second time and the condenser tube was broken with a hammer to remove the beautiful white crystal crust. Some of the PH_4I was allowed to stand over the summer in a glass stoppered bottle. When the writer returned, the PH_4I had departed and in its place was a liquid containing some white crystals as a precipitate. The PH_4I had decomposed on exposure to the moisture in the air, giving of PH_3 and leaving acids of phosphorus in solution, and some had apparently crystallized out.

In order to continue the investigation the PH_4I was prepared a third time and it was found possible to scratch the crystals loose with a glass rod so that no more apparatus need be broken. It was then placed in bottles sealed with paraffin. No matter how many times it was coated with paraffin there was always one gas-hole left when the paraffin had cooled. The paraffin was also tinted brown.

The first time phosphine was prepared, apparatus was set up as per fig.2 The apparatus was found inadequate for keeping all the phosphine evolved so it was prepared twice more using the modified apparatus as shown in fig.3 Natural gas was used in place of hydrogen to replace the air in the entire apparatus. The gas was allowed to pass through the apparatus for several hours before beginning the generation of the phosphine. The T-tube near the phosphine generator, dipped into mercury, was used as a safety-valve in case the tubes farther on should freeze and therefore prevent the passage of the phosphine and other gases generated. Flask B served as a water condenser. It was found, in the first attempt to prepare phosphine that a yellow solid crystallized in most of the apparatus. So the first Dewar, containing liquid air, served to freeze everything that came over it, and D_1 and D_2, containing liquid ammonia, were used so that this yellow solid would be formed in the T_1 and T_2 when the gases passed over, upon removing D_1 and allowing T_2 to warm gradually. Excess water vapor was held back in T_3 because the temperature of T_3 was never allowed to reach the boiling point of water.

Previously the entire system from X to X′ was thoroughly dried by drawing dry air through the apparatus and heating all of the apparatus, except the Dewars, for several hours. It was concluded that all the liquid which was collected in T_4 was liquid phosphine. When sufficient phosphine had been produced to make a test, phosphonium iodide which had previously been placed in the arm of T_4 was gently pushed, a small quantity at a time, by a small glass piston P, into the liquid phosphine. It will be noted that this phosphonium iodide was cooled as in the ammonia experiment so that the temperature of solute and solvent was practically the same. With every addition of the phosphonium iodide, gas was evolved, which indicated that the phosphonium iodide had been decomposed; so it was concluded that the phosphine could not be used as a conducting solvent.

Gengembre prepared a compound of phosphorus and hydrogen in 1783 which was spontaneously inflammable. Pelletier, and afterwards Davy, prepared a very similar gas by heating phosphoric acid. This gas differed from the other in being non-spontaneously inflammable. Paul Thenard gave the true explanation of the difference between these two gases. He showed that the spontaneous inflammation of the one gas was due to the presence in it of small traces of the vapor of liquid hydride of phosphorus. The non-spontaneously inflammable phosphine may be prepared by warming phosphorus with an alcoholic solution of potash or by decomposing calcium phosphide by means of hydrochloric acid. Pure phosphine is also produced by the action of water or a very dilute sulphuric acid on aluminum phosphide.[14]

Phosphine is a colorless gas, smelling like spoiled fish. It liquifies at -85°C., solidifies at -133.5°C, and has a critical temperature 52.8° and critical pressure 64 atmospheres. The pure gas takes fire only above a temperature of 100°, but is so inflammable that the heat evolved by the friction of the stopper on opening the bottle containing the gas is sometimes sufficient to produce its inflammation.[15] It may be mixed with oxygen without undergoing any alteration, but if this mixture is suddenly exposed to diminished pressure

[14] Roscoe and Schor., I, pp. 619-620
[15] Ibid., I, p. 622

The Preparation of Hydrogen Iodide
From the Elements
Fig. 4

G - Hydrogen generator
W_1 -
W_2 - Woulff bottle with H_2SO_4 as dehydrater
W_3 -
T_1 - T-tube for controlling valve
F - Solid iodine container
C - $CaCl_2$ tube containing Pt catalyzer
T_2 - Condenser for solid HI
T_3 - Condenser for liquid HI
E_1 - Electrodes
P_1 - Piston
R - Rheostat
A - Ammeter
E_2 - Source of direct current
P_2 - Pyrex combustion tube used to replace $CaCl_2$ tube. This tube also held the solid iodine in place of F

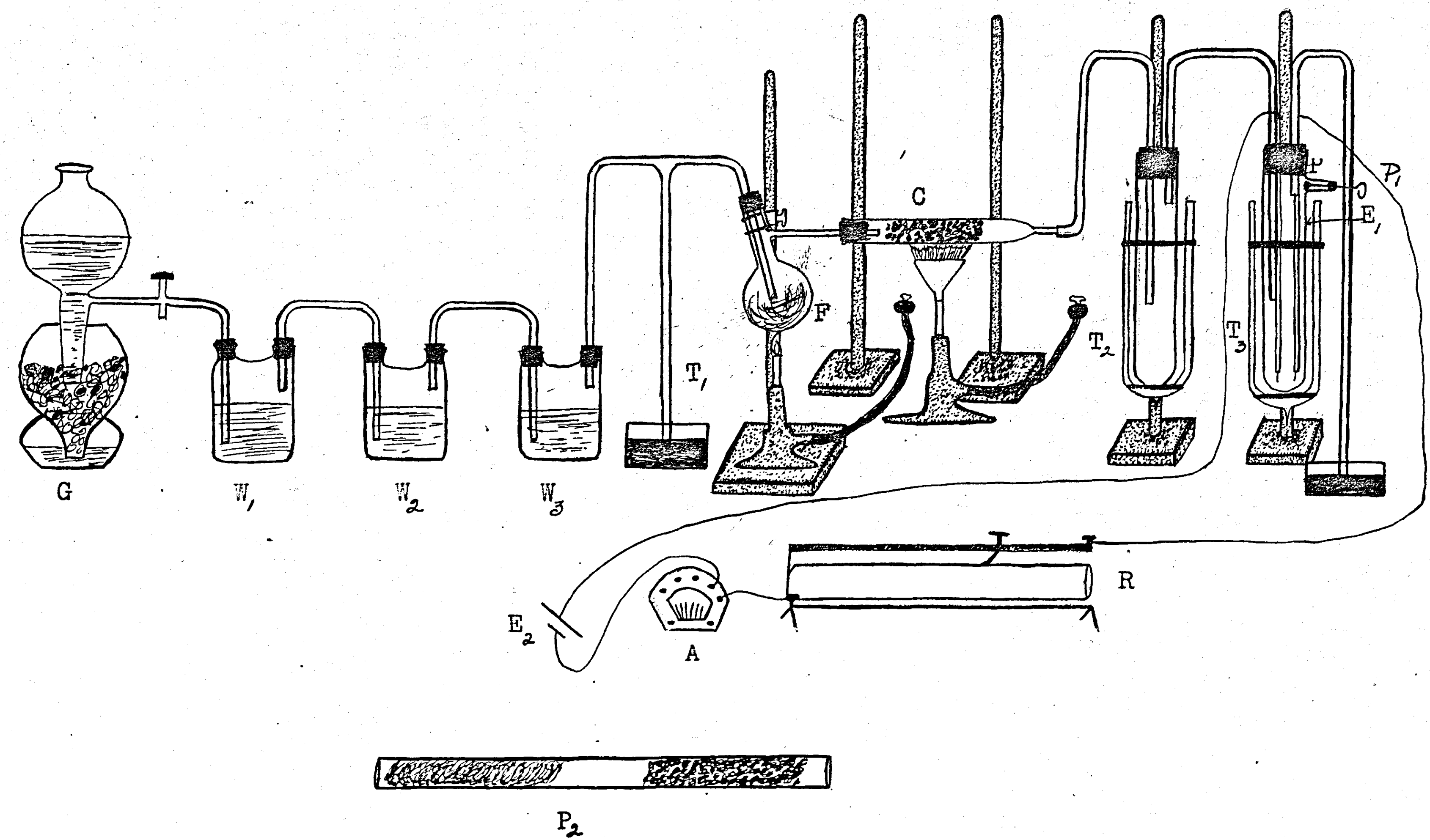


Fig. 4

an explosion occurs.[16] Phosphine decomposes into phosphorus and hydrogen by means of the electric spark. The volume of hydrogen being three to two volumes of phosphorus.[17] Phosphine is similar to ammonia in its formula and slightly like it in its properties.[18] It combines like ammonia, with certain metallic chlorides. For example, with aluminum chloride, stannic, titanium, and antimony chlorides.[19] It is a very poisonous gas. It possesses the power of combining with the respiratory oxygen linked to haemogloblin, but its toxic action appears to be almost entirely due to more complex operations. It is feebly basic and combines with HBr and HI to form salts in a manner similar to ammonia.[20] These salts contain the compound radical PH_4 which is usually termed phosphonium, just as the compound radical NH_3 is termed ammonium. PH_4I and PH_4Br are formed when PH_3 dissolves in concentrated HI and HBr. It was mentioned previously that an orange yellow solid was formed in several of the tubes along with phosphine.[21] Stock, Böttcher, and Lang prepared an orange compound of hydrogen and phosphorus which wase a solid having the formula P_9H_2. Ependa prepared a yellow compound having the formula $P_{12}H_6$. The compound which I obtained is probably one of these.

Hydrogen Iodide, HI[22]
(Jodwasserstoff, HJ)

Jodwasserstoffsäure, Acidum hydrojodicum.

I. Gaseous Hydrogen Iodide
1. From the Elements.

Hydrogen iodide can be prepared in the same manner as hydrogen bromide according to H. and W. Biltz. For this purpose one drys the H_2 by passing it through three H_2SO_4 wash bottles from the Kipp generator and leads it by means of a tube into the bulb of a little fractionating flask which contains 50 grams I_2 and is gently warmed. The short distillation tube of the fractionator is connected by a cork to a long, wide distillation tube 70 cm. in length. Not far from the entrance is a platinized, asbestos pad which is heated by a broad flame. (During the reaction the I_2 is not deposited in the farther part of the tube.) The gaseous mixture is washed through very little H_2O into a wash bottle prepared

[16] Roscoe and Schor. I, p. 622
[17] Ibid., p. 622
[18] Inorganic Chem. p. 263
[19] Roscoe and Schor., I, p.622
[20] Inorganic, p. 264
[21] This experiment, p. 8
[22] Handbuch: Vanino, p. 60-61

from a test-tube and can be drawn into the small bottles connected in series. From the beginning of the experiment the apparatus is filled with H_2 as for HBr preparation.

2. From Iodine, Phosphorus, and Water.

According to Lothar Meyer it is expedient to bring together an excess of I_2 with phosphorus and water, just as the other directions require. If I_2 and H_2O react with an excess of phosphorus, in the last part of the process the very troublesome formation of PH_3 can not be avoided. It is best therefore to use the amounts corresponding to the equation:

$$P + 5I + 4H_2O = H_3PO_4 + 5HI$$

about 100 grams I_2, 5 grams phosphorus, and a little more water (20 grams instead of 12 grams.) The I_2 is placed in an upturned tubulated retort and moistened with about 10 grams H_2O. With the other half of the H_2O the red P is mixed to a thin paste which is dropped in through a dropping funnel, which is closed by a stopcock, with a long, not too thick, glass tube ground to a point. Now let a drop of the P mixture fall upon the I_2 through a careful upward movement, wait for the entering reaction and then gradually add more P in small portions. In this manner the evolution of the gas can result calmly, whereas an explosion would take place by the rapid addition of the P mixture.

The I_2 carried over by the HI deposits itself completely in the neck of the retort. In order to hold it back completely it is well to connect the retort with the receiver through an oblique, upturned, long, straight, not too narrow, glass tube; and finally wash the gas through a little H_2O located in a U-tube. When the generation first slackens, warm it gently; water is also volatilized, which carries down the I_2 clinging to the walls. If the I_2 color should not disappear after further heating, one adds a little P. When no more gas is generated, distill the aqueous acid. From the amount used one obtains 74.4 grams gaseous acid and 23.7 grams through distillation; by addition of 35 grams H_2O, 47.5 grams gaseous acid and 57.3 grams through distillation.[23]

[23] Handbuch: Vanino, I, p. 61

Properties: HI is a colorless, strong acid. Specific gravity, 4.3757; on exposure to the air it forms large white clouds. It smells like HCl and has a choking effect when inhaled. By heating to 180°C. HI begins to decompose into its elements. It is very easily soluble in H_2O.[24]

Hydrogen iodide was first made from the elements using apparatus as shown in fig.4 It will be noted that a pyrex calcium chloride tube containing platinum gauze and heated by means of a bunsen burner with a wing top to give a hot flame, evenly distributed, was used as a chamber for the union of the gaseous hydrogen and the iodine vapor to form gaseous hydrogen iodide, which was then led into a tube surrounded by liquid air. In this tube everything that came over was frozen. The next Dewar contained liquid ammonia which served to condense the hydrogen iodide when the liquid air Dewar had been lowered sufficiently to raise the temperature of the substances in tube T_2, a trifle above the boiling point of hydrogen iodide. The first attempt to prepare HI was not very successful, due to the fact that the iodine was heated too rapidly and thus all of it was not given time to unite with the hydrogen when passed over the platinum catalyst. Therefore, the tubes beyond the catalyst became plugged with the beautiful iodine crystals. The $CaCl_2$ tube and the tube leading into T_2, as well as the small distilling flask, were removed, and in their place were substituted a long, thick, pyrex combustion tube and a clean, small, glass tube to lead the gas from the combustion tube to T_2. Iodine crystals were then placed near the entrance of the pyrex tube, and filled it about one-third full. The opposite end of the tube was filled for about 10 cm. with platinum asbestos. When the whole system was thoroughly saturated with hydrogen the platinum asbestos was strongly heated with the wing top burner, and the iodine nearest the platinum was gently heated at the same time, while a steady flow of hydrogen passed through the tube. In this manner a yield of hydrogen iodide, sufficient to make a good test, was obtained. However, the yield was very small for a half-day's labor.

[24] General Chemistry, p. 152

When the liquid hydrogen iodide had been condensed in T_3 a small amount of phosphonium iodide was first cooled by means of liquid air and was then pushed through the sides of the tube by means of small gas piston P_1. It was noted that no evolution of gas occurred upon the addition of the iodide, nor did it occur on the subsequent addition of this salt in several small quantities. The wires leading to the electrodes were then connected with rheostat, ammeter, and direct current. At first there was no deflection of the needle. The resistance was then removed and the wires changed to detect any minute quantity, and after connecting it repeatedly so that smaller and smaller currents could be measured, there was finally a deflection of the needle. A milliammeter was then connected and it showed a current of three milliamperes.

Dr. Cady suggested that since the tube was surrounded by liquid ammonia, it might be possible that the NH_3 might have produced a salt which would be responsible for this current, so it was necessary to again make the hydrogen iodide in the absence of NH_3. We decided to try the second method for the preparation of HI, using iodine, phosphorus, and water. It will be noted that Lothar Meyer suggested 20 grams of water should be used instead of 12 in the proportions given, so this method was tried. The iodine and part of the water was placed in the retort and chilled in ice water, while a mixture of phosphorus and the remainder of the water was run in through a dropping funnel. The ice water was then removed and the contents of the retort allowed to warm up gradually. The result was that there was only a smell of HI in the tube surrounded by liquid air, while in the calcium chloride tube which was used as a water condenser, there was so much water that it served to absorb all the HI which came over. Therefore, this method was modified. The retort was cleaned and dried and 200 grams of iodine and 20 grams of phosphorus were placed in the retort which had been thoroughly chilled with ice water and then just the calculated[25] amount of water was added drop by drop, waiting each time for the evolution of the gas to diminish. This time, before the ice bath was removed, a large quantity of solid, white HI collected in the tube surrounded by liquid air.

[25]Calculated from the equation:

$$5I + 9P + 16H_2O = 5PH_4I + 4H_3PO_4$$

The ice bath was removed and gradually a considerable quantity of frozen HI collected. The liquid air Dewar was then removed and sufficient HI to test was allowed to distill over into the second tube surrounded by liquid air. The phosphonium iodide was cooled and dropped into the HI while it was thawing out. Its conductivity was measured, and at first no current passed, but when all the solid had been changed to liquid the needle of the ammeter began to move, and moved farther and farther across the milliammeter until it bent the needle against the side opposity zero. The HI was then allowed to vaporize and pass off an d a salt remained in the tube which had all the appearance of phosphonium iodide and effervesced very strongly when water was poured upon it, and decomposed, proving it to be PH_4I. Thus it was proved that PH_4I quietly dissolves in liquid HI and that it must ionize, because it conducts a current when dissolved in liquid HI.

The liquid HI, when pure, is colorless like water. The HI with which I worked was a very delicate pink, which I presumed to be colored with very little free iodine. Upon passage of a current the solution gradually turned to a deep brown, indicating that iodine must have been liberated at one of the electrodes. The electrodes were so close together that it was impossible to detect at which electrode this liberation took place. I hope to ascertain what is liberated at each electrode in the near future.

B. Courtois, 1813, first prepared HI without recognizing its nature. Hydrogen does not unite with iodine at ordinary temperatures. J.L. Gay Lussac, 1814, showed that if hydrogen and iodine vapor are passed through a red hot tube, union does occur. Davy also prepared Le Gaz de l'iode, and E. Turner showed in 1824 that the reaction occurs at ordinary temperatures in the presence of a platinum catalyzer. P. Hautefeuille, 1867, said that combination is only partial because the same catalytic agent decomposes HI, proving the reaction to be reversible.[26] A little HI is formed if iodine water is exposed to sunlight, or when heated, according to the equation:

$$2H_2O + 2I = 4HI + O_2$$

[26] J. W. Mellor, A. Comprehensive Treatise on Inorganic and Theoretical Chemistry, II, 1922, p. 170

Hydrogen iodide is a colorless gas at ordinary temperatures. It fumes strongly in moist air, has an irritating odor, and an acid taste. It is a colorless liquid which has a boiling point of -34.14 C. at 730.4 mm., and -34.12°C at 739.8 mm. pressure. The white crystalline solid hydrogen iodide melts at -50.8 C. Liquid HI has a specific conductivity equal to 0.2 x 10.[27] HI is much heavier than air, having a molar weight of 128. Although a poor conductor of electricity, when water is added to the acid it becomes an excellent conductor, being as active as an HCl solution containing an equal number of gram moles per liter.[28] When a colorless solution of HI is exposed to the air it quickly turns brown due to the reaction:

$$4HI + SO_2 = 2H_2O + 2I_2$$

It forms a trihydrate, HI $3H_2O$, or a tetrahydrate HI $4H_2O$.[29] During the generation of the HI in my experiment a red solid collected on the walls of both mercury receivers. This solid turned yellow upon heating. The mercury had reacted with the HI to form mercuric iodide.

This series of investigations was begun upon the suggestion of Dr. Cady, that no information was available concerning the ionization of phosphonium iodide; and since "Die Begeisterung ist nicht wie ein Herring die man auf einiger Jahren einpickeln kann;" and also "Enthusiasmus is wie ein Ei; es muss frisch gegessen werden".[30] I at once began my investigations. I had intended to try liquid hydrogen fluoride also, but at present we have not the necessary platinum still and platinum containers to use for such preparation. It would also be interesting to use various other liquids such as sulphur dioxide and hydrogen sulphide.

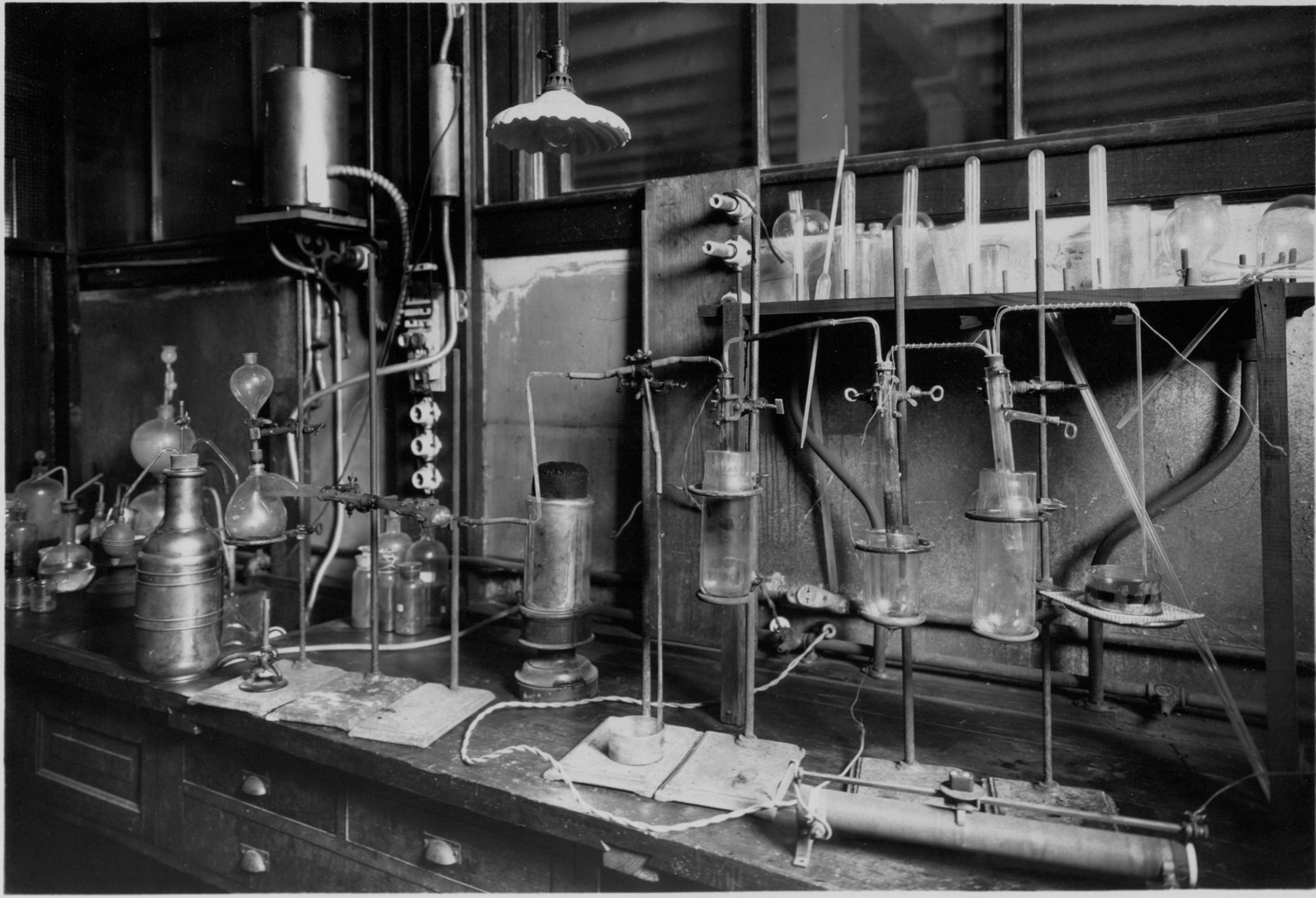
[27] Comp. Treatise, II, p. 179
[28] General Chem., p. 152
[29] R. Friedlander und Sohn, Berichte der Deutschen Chemischen Gesellschaft, 1893, XXVI, p. 2307
[30] Source: Prof. H. Werner, State Food Lab. , Kansas.

The Research Room

Apparatus Set Up For
The Preparation of Hydrogen Iodide
From Iodine, Phosphorus, and Water

The retort contained red phosphorus and iodine, into which water had been run while the retort was cooled in ice water, and after the evolution of HI ceased the ice bath was removed and the retort was heated gently. The calcium chloride tube serves as a water condenser, as does also the tube immersed in the first cooler which contains ice, water, and salt. The second and third Dewars contain liquid air. The T-tube, dipping in the Hg, serves as a pressure guage. The electrodes are minute tubes through which platinum wires were sealed and the connecting wires dipped into Hg which partially fills the tubes and forms contact with the platinum.

The side tube connected with the last pyrex test tube held the phosphonium iodide which was pushed into the liquid hydrogen iodide by means of the small glass piston. Note the dark color of the water solution above the Hg in the last crystallizing dish. It was colored brown, and a bright red solid was formed above it on the sides of the dish. This was also the case in the other crystallizing dish, although not so noticeable in the picture. The large Dewar with bulb tube attached contains liquid air. The other large Dewar served to keep the hydrogen iodide solid over night when the Dewar was filled with liquid air. Hydrogen iodide is so volatile that it was necessary to cover every joint with paraffin.



BIBLIOGRAPHY

Annalen dar Chemie. Herausgegeben von A. Kekulè, E. Erlenmeyer und J. Volhard, Leipzig, C. F. Wintersche Verlagshandlung, 1870.

Berichte der Deutschen Chemischen Gesellschaft. Eigentun der Deutschen Chemischen Gesellschaft. Commissionsverlag von R. Friedlander und Sohn, Berlin, Redacteur; Ferd. Tiemann. Stellvertretender Redacteur: F. v. Dechend, 1904.

Chemical News and Journal of Physical Science, v. Edited by Wm. Crookes, F. R. S., London, published at the Office, Boy Court, Ludgate Hill, E. C., 1889.

Chemisches Central - Blatt. Herausgegeben von der Deutschen Chemischen Gesellschaft. Redigiert von Dr. Albert Hesse, Berlin, Commissions-Verlag von R. Friedlander und Sohn, 1904.

Comprehensive Treatise on Inorganic and Theoretical Chemistry, A. By J. W. Mellor, D. Sc. Vol. II, London, Longmans, Green and Company, 39 Paternoster Row, 1922.

General Chemistry. By Hamilton P. Cady, Ph.D. First Edition, New York, McGraw-Hill Book Company, 1916.

Gmelin-Kraut's Handbuch der anorganischen Chemie Herausgegeben von C. Friedheim. Heidelberg, Carl Winter's Universitätsbuchhandlung, 1907.

Handbuch der Präparativen Chemie. Herausgegeben von Professor Dr. Ludwig Vanino, Zwei Bande, Anorganischer Teil. Stuttgart Verlag von Ferdinand Enke, Stuttgart, 1921.